


FORM PTO-1390 (REV 5-93)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE	ATTORNEY'S DOCKET NUMBER 2215/50186
<b>TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371</b>			U.S. APPLICATION NO. (if known, see 37 CFR 1.5) <b>09/890529</b>
INTERNATIONAL APPLICATION NO. PCT/US00/02445	INTERNATIONAL FILING DATE 31 January 2000	PRIORITY DATE CLAIMED 1 February 1999	
TITLE OF INVENTION SINGLE COMPONENT SULFUR-BASED CATHODES FOR LITHIUM AND LITHIUM-ION BATTERIES			
APPLICANT(S) FOR DO/EO/US			
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:			
<p>1. <input checked="" type="checkbox"/> This is a <b>FIRST</b> submission of items concerning a filing under 35 U.S.C. 371.</p> <p>2. <input type="checkbox"/> This is a <b>SECOND</b> or <b>SUBSEQUENT</b> submission of items concerning a filing under 35 U.S.C. 371.</p> <p>3. <input type="checkbox"/> This express request to begin national examination procedures (35 U.S.C. 371(f) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).</p> <p>4. <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.</p> <p>5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)).</p> <p style="margin-left: 40px;">a. <input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau).</p> <p style="margin-left: 40px;">b. <input type="checkbox"/> has been transmitted by the International Bureau</p> <p style="margin-left: 40px;">c. <input checked="" type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US)</p> <p>6. <input type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)).</p> <p>7. <input type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).</p> <p style="margin-left: 40px;">a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau).</p> <p style="margin-left: 40px;">b. <input type="checkbox"/> have been transmitted by the International Bureau.</p> <p style="margin-left: 40px;">c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.</p> <p style="margin-left: 40px;">d. <input type="checkbox"/> have not been made and will not be made.</p> <p>8. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).</p> <p>9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)) - Unexecuted</p> <p>10. <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).</p> <p><b>Item 11. to 16. below concern other document(s) or information included:</b></p> <p>11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</p> <p>12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</p> <p>13. <input checked="" type="checkbox"/> A <b>FIRST</b> preliminary amendment.</p> <p style="margin-left: 40px;"><input type="checkbox"/> A <b>SECOND</b> or <b>SUBSEQUENT</b> preliminary amendment.</p> <p>14. <input type="checkbox"/> A substitute specification.</p> <p>15. <input type="checkbox"/> A change of power of attorney and/or address letter.</p> <p>16. <input checked="" type="checkbox"/> Other items or information: 6 (Six) Sheets of Formal Drawings</p>			

U.S. APPLICATION NO (if known, see 37 CFR 1.5) <b>09/890529</b>		INTERNATIONAL APPLICATION NO PCT/US00/02445		ATTORNEY'S DOCKET NUMBER 2215/50186			
17. <input type="checkbox"/> The following fees are submitted: Basic National Fee (37 CFR 1.492(a)(1)-(5)):  Search Report has been prepared by the EPO or JPO ..... \$860.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) ... \$690.00 No international preliminary examination fee paid to USPTO (37 CFR 1.482)  but international search fee paid to USPTO (37 CFR 1.445(a)(2)) ..... \$710.00 Neither international preliminary examination fee (37 CFR 1.482) nor  international search fee (37 CFR 1.445(a)(2) paid to USPTO ..... \$1000.00 International preliminary examination fee paid to USPTO (37 CFR 1.482)  and all claims satisfied provisions of PCT Article 33(2)-(4) ..... \$100.00  <b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>				CALCULATIONS		PTO USE ONLY	
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$ 130.00			
Claims	Number Filed	Number Extra	Rate				
Total Claims	42-20=	22	X \$18.00	\$ 396.00			
Independent Claims	8-3=	5	X \$80.00	\$ 400.00			
Multiple dependent claims(s) (if applicable)			+ \$260.00	\$			
<b>TOTAL OF ABOVE CALCULATIONS =</b>				\$1,786.00			
Reduction by 1/2 for filing by small entity, if applicable. Verified Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28).				\$ 893.00			
<b>SUBTOTAL =</b>				\$ 893.00			
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$			
<b>TOTAL NATIONAL FEE =</b>				\$ 893.00			
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28,3.31). \$40.00 per property +				\$			
<b>TOTAL FEE ENCLOSED =</b>				\$ 893.00			
				Amount to be:		\$	
				refunded			
				charged		\$	
a. <input checked="" type="checkbox"/> One check in the amount of \$893.00 for the filing fee is enclosed b. <input type="checkbox"/> Please charge my Deposit Account No. _____ in the amount of \$_____ to cover the above fees. A duplicate copy of this sheet is enclosed. c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees, which may be required, or credit any overpayment to Deposit Account No. <u>05-1323</u> . A duplicate copy of this sheet is enclosed.							
NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.							
SEND ALL CORRESPONDENCE TO: Crowell & Moring, L.L.P. P.O. Box 14300 Washington, D.C. 20044-4300 Tel. No. (202) 628-8800 Fax No. (202) 628-8844				 SIGNATURE William G. Ackerman NAME 45,320 REGISTRATION NUMBER August 1, 2001 DATE			

Attorney Docket: 2215/50186  
PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: JOHN POPE ET AL.

International Application No.: PCT/US00/02445

Filed: August 1, 2001 Examiner: Not Assigned

Title: SINGLE COMPONENT SULFUR-BASED CATHODES FOR LITHIUM  
AND LITHIUM-ION BATTERIES

PRELIMINARY AMENDMENT

Box PCT  
Commissioner for Patents  
Washington, D.C. 20231

August 1, 2001

Sir:

Prior to examination and calculation of fees, please  
preliminarily amend the above-identified application as follows:

IN THE CLAIMS

Please amend claims 1-26 as follows:

1. (Amended) A method of selecting cathode materials for  
a sulfur-based Lithium battery having a cathode which has a  
conducting polymer and a sulfur species, comprising:

identifying a characteristic of the conducting polymer;

identifying a characteristic of the sulfur species;

evaluating the characteristic of the conducting polymer  
and the sulfur species;

selecting the conducting polymer and the sulfur species  
based on the identified characteristic;

09/890529

wherein the identified characteristic of the sulfur species and the identified characteristic of the conducting polymer are at least one characteristic selected from one of:

ionically conductive for  $\text{Li}^+$  ions;

inherent charge capacity above 230 Ah/kg;

substantial overlap of thermodynamic potentials of the sulfur species and the conducting polymer;

electronic conductivity above  $10^{-4}$  S/cm of the cathode materials;

no solubility in electrolyte solutions; and

a capacity fade of less than 10% when the cathode material is cycled 100 times.

2. (Amended) The method according to claim 1, wherein the identified characteristics are all of the at least one characteristics.

3. (Amended) The method according to claim 1, wherein the at least one characteristic is substantial overlap of thermodynamic potentials of the sulfur species and the conducting polymer.

4. (Amended) The method according to claim 1, wherein the at least one characteristic is no solubility in electrolyte solutions.

5. (Amended) A cathode material for use in a sulfur-based Lithium battery comprising a sulfur species and a conducting polymer;

wherein the conducting polymer and the sulfur species exhibit at least one characteristic selected from one of:

ionically conductive for  $\text{Li}^+$  ions;

charge capacity above 230 Ah/kg;

substantial overlap of thermodynamic potentials of the sulfur species and the conducting polymer;

electronic conductivity above  $10^{-4}$  S/cm of the cathode materials;

no solubility in electrolyte solutions; and

a capacity fade of less than 10% when the cathode material is cycled 100 times.

6. (Amended) The cathode material according to claim 5, wherein the at least one characteristic includes all of the characteristics of:

ionically conductive for  $\text{Li}^+$  ions;

inherent charge capacity above 230 Ah/kg;

substantial overlap of thermodynamic potentials of the sulfur species and the conducting polymer;

electronic conductivity above  $10^{-4}$  S/cm of the cathode materials;

no solubility in electrolyte solutions; and

a capacity fade of less than 10% when the cathode material is cycled 100 times.

7. The cathode material according to claim 5, wherein the at least one characteristic is substantial overlap of

thermodynamic potentials of the sulfur species and the conducting polymer.

8. (Amended) The cathode material according to claim 5, wherein the at least one characteristic is substantial overlap of thermodynamic potentials of the sulfur species and the conducting polymer and no solubility in electrolyte solutions.

9. (Amended) A cathode material for use in a sulfur-based Lithium battery containing an electrolyte comprising, a sulfur species and a conducting polymer, wherein the conducting polymer is a single component sulfur-based conducting polymer with the sulfur species covalently linked to the conducting polymer.

10. (Amended) The cathode material according to claim 9, wherein the covalent link of the sulfur species and the conducting polymer provides suitable fade characteristics by not allowing the sulfur species to be soluble in the electrolyte.

11. (Amended) The cathode material according to claim 9, wherein the battery contains no other sulfur or other sulfur species except for the linked sulfur species.

12. (Amended) The cathode material according to claim 9, wherein the cathode material is a thiophene based polymer with the covalently linked sulfur species.

13. The cathode material according to claim 9, wherein the conducting polymer is covalently-derivatized with sulfides or sulfide-containing groups.

14. (Amended) A cathode material for use in a sulfur-based Lithium battery containing an electrolyte comprising, a sulfur species including sulfide components and a conducting polymer, wherein the conducting polymer is a single component sulfur-based conducting polymer; and

wherein physical constraints of the conducting polymer and the sulfide components are provided via covalent bonds which are present regardless of charge state of the cathode material.

15. (Amended) An electric current producing cell comprising:

an anode;

a cathode containing a cathode material of claim 14;

and

an electrolyte between the anode and cathode.

16. (Amended) An electric current producing cell comprising:

an anode;

a cathode containing a cathode material of claim 12;

and

an electrolyte between the anode and cathode.

17. (Amended) An electric current producing cell comprising:

an anode;

a cathode containing a cathode material; and

an electrolyte between the anode and cathode;

wherein the cathode material includes a conduction polymer and a sulfur species which exhibit characteristics of:

ionically conductive for  $\text{Li}^+$  ions;

inherent charge capacity above 230 Ah/kg;

substantial overlap of thermodynamic potentials of the sulfur species and the conducting polymer;

electronic conductivity above  $10^{-4}$  S/cm of the cathode materials;

no solubility in electrolyte solutions; and

a capacity fade of less than 10% when the cathode material is cycled 100 times.

18. (Amended) The cathode material according to claim 13, wherein the sulfur-derivatized conducting polymer is represented by a formula  $(R_i)_n(Y_jA_k)_{mL}$  wherein R is monomer or oligomer units of the conducting polymer, i is 1 to n and n is greater than 20, Y is a functionalizing group that provides additional physical or chemical properties to the conducting polymer and j is 0 to n; A is the sulfur species, k is 1 to n and m is 1 to 12.

19. (Amended) The cathode material according to claim 18, wherein n is greater than 1000.

20. (Amended) The cathode material according to claim 19, wherein n is greater than 100,000.

21. (Amended) The cathode material according to claim 13, wherein the sulfur-derivatized conducting polymer represented by a formula  $(R)_n(YS_m)_{xL}$  wherein R is a conducting polymer backbone



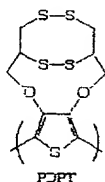
and n is greater than 20; Y is a functionalizing group; S is an organosulfur moiety, m is 1 to 12 and x is 1 to 4.

22. (Amended) The cathode material according to claim 21, wherein n is greater than 1000.

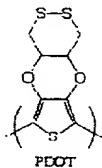
23. (Amended) The cathode material according to claim 22, wherein n is greater than 100,000.

24. (Amended) The cathode material according to claim 21, wherein R is polythiophene or derivatives thereof.

25. (Amended) The cathode material according to claim 24, wherein the single component sulfur-based conducting polymer is represented by:



26. (Amended) The cathode material according to claim 24, wherein the single component sulfur-based conducting polymer is represented by:



Please add the following new claims:

-- 27. (New) The cathode material according to claim 18, wherein the functionalizing group Y includes at least one ionically conducting functional group of poly(ethylene oxide) or derivatives thereof.

28. (New) The cathode material according to claim 18, wherein the functionalizing group Y includes at least one redox species or aggregates of redox species.

29. (New) The cathode material according to claim 24, wherein said Y is ethoxy.

30. (New) The cathode material according to claim 24, wherein said Y is a functional group having an electron-donating character of ethoxy.

31. (New) The cathode material according to claim 29, wherein said S is thiolate.

32. (New) The cathode material according to claim 29, wherein said S is a sulfur species having a redox functionality of thiolate.

33. (New) The cathode material according to claim 31, wherein each said R is substituted by at least two of said Y, at least two said S, or at least two of said Y and said S.

34. (New) The cathode material according to claim 31, wherein an additional Y is an ion-conducting functional group of poly(ethylene oxide) or derivatives thereof.

35. (New) The cathode material according to claim 21, wherein said R is one of polypyrrole, polyaniline, polyacetylene, and a derivative thereof.

36. (New) A method of making a sulfur-based Lithium battery having a cathode which has a conducting polymer and a sulfur species; comprising:

identifying a characteristic of the conducting polymer;

identifying a characteristic of the sulfur species;

evaluating the characteristic of the conducting polymer and the sulfur species;

selecting the conducting polymer and the sulfur species based on the identified characteristic;

providing the selected conducting polymer and the sulfur species;

providing an anode; and

providing an electrolyte between the anode and the cathode;

wherein the identified characteristic of the sulfur species and the identified characteristic of the conducting polymer are at least one characteristic selected from one of:

ionically conductive for  $\text{Li}^+$  ions;

inherent charge capacity above 230 Ah/kg;

substantial overlap of thermodynamic potentials of the sulfur species and the conducting polymer;

electronic conductivity above  $10^{-4}$  S/cm of the cathode materials;

no solubility in electrolyte solutions; and

a capacity fade of less than 10% when the cathode material is cycled 100 times.

37. (New) The method according to claim 36, wherein the identified characteristics are all of the at least one characteristics.

38. (New) The method according to claim 36, wherein the at least one characteristic is substantial overlap of thermodynamic potentials of the sulfur species and the conducting polymer.

39. (New) The method according to claim 36, wherein the at least one characteristic is no solubility in electrolyte solutions.

40. (New) the method according to claim 36, wherein the sulfur species is electroactive.

41. (New) The cathode material according to claim 14, wherein the conducting polymer has no labile protons.


42. (New) The cathode material according to claim 14, wherein the conducting polymer is functionalized in order to change conductivity or thermodynamic potential to overlap a conductivity or thermodynamic potential of the sulfur species.

REMARKS

If there are any questions regarding this amendment or the application in general, a telephone call to the undersigned would be appreciated since this should expedite the prosecution of the application for all concerned.

If necessary to effect a timely response, this paper should be considered as a petition for an Extension of Time sufficient to effect a timely response, and please charge any deficiency in fees or credit any overpayments to Deposit Account No. 05-1323 (Docket #2215/50186).

Respectfully submitted,

  
William G. Ackerman  
Registration No. 45,320

CROWELL & MORING, LLP  
P.O. Box 14300  
Washington, DC 20044-4300  
Telephone No.: (202) 628-8800  
Facsimile No.: (202) 628-8844

WGA:sbh

09/890529

Attorney Docket No. 2215/50186  
PCT/US00/02445MARKED-UP COPY OF AMENDMENTS

1. (Amended) A method of selecting cathode materials for a sulfur-based Lithium battery [wherein the] having a cathode [comprises] which has a conducting polymer and a sulfur species[;], comprising:

identifying a characteristic of the conducting polymer;

identifying a characteristic of the sulfur species;

evaluating the characteristic of the conducting polymer and the sulfur species;

selecting the conducting polymer and the sulfur species based on the identified characteristic;

wherein the identified characteristic of the sulfur species and the identified characteristic of the conducting polymer are at least one characteristic selected from [the group consisting] one of: [ease of fabrication using straightforward synthetic procedures;]

ionically conductive for Li<sup>+</sup> ions; [a high density of electroactive species per weight and volume/large]

inherent charge capacity [>] above 230 Ah/kg;

[good] substantial overlap of thermodynamic potentials of the sulfur species and the conducting polymer;

[reasonable] electronic conductivity above [(10<sup>-4</sup> S/cm[])] of the cathode materials;

no solubility in electrolyte solutions; and

[or electrochemically stable to many repeated charge and discharge cycles/] a capacity fade of less than 10% when the cathode material is cycled [1000] 100 times.

2. (Amended) The method [of] according to claim 1, wherein the identified characteristics are all of the at least one characteristics.

3. (Amended) The method [of] according to claim 1, wherein the at least one characteristic is [good] substantial overlap of thermodynamic potentials of the sulfur species and the conducting polymer.

4. (Amended) The method [of] according to claim 1, wherein the at least one characteristic is no solubility in electrolyte solutions.

5. (Amended) A cathode material for use in a sulfur-based Lithium battery comprising a sulfur species and a conducting polymer;

wherein the conducting polymer and the sulfur species exhibit at least one characteristic selected from [the group consisting] one of: [ease of fabrication using straightforward synthetic procedures;]

ionically conductive for Li<sup>+</sup> ions;

[a high density of electroactive species per weight and volume/large inherent] charge capacity [>] above 230 Ah/kg;

[good] substantial overlap of thermodynamic potentials of the sulfur species and the conducting polymer;

[reasonable] electronic conductivity above  $[>10^{-4}]$  S/cm of the cathode materials;

no solubility in electrolyte solutions; and

[or electrochemically stable to many repeated charge and discharge cycles/]a capacity fade of less than 10% when the cathode material is cycled [1000] 100 times.

6. (Amended) The cathode material [of] according to claim 5, wherein the at least one characteristic includes all of the characteristics [from the group consisting] of: [ease of fabrication using straightforward synthetic procedures;]

ionically conductive for  $\text{Li}^+$  ions;

[a high density of electroactive species per weight and volume/]large inherent charge capacity [ $>$ ] above 230 Ah/kg;

[good] substantial overlap of thermodynamic potentials of the sulfur species and the conducting polymer;

[reasonable] electronic conductivity above  $[>10^{-4}]$  S/cm of the cathode materials;

no solubility in electrolyte solutions; and

[or electrochemically stable to many repeated charge and discharge cycles/]a capacity fade of less than 10% when the cathode material is cycled [1000] 100 times.

7. The cathode material [of] according to claim 5, wherein the at least one characteristic is [good] substantial overlap of thermodynamic potentials of the sulfur species and the conducting polymer.



8. (Amended) The cathode material [of] according to claim 5, wherein the at least one characteristic is [good] substantial overlap of thermodynamic potentials of the sulfur species and the conducting polymer and no solubility in electrolyte solutions.

9. (Amended) A cathode material for use in a sulfur-based Lithium battery containing an electrolyte comprising, a sulfur species and a conducting polymer, wherein the conducting polymer is a single component sulfur-based conducting polymer with the sulfur species covalently linked to the conducting polymer.

10. (Amended) The cathode material [of] according to claim 9, wherein the covalent link of the sulfur species and the conducting polymer provides suitable fade characteristics by not allowing the sulfur species to be soluble in the electrolyte.

11. (Amended) The cathode material [of] according to claim 9, wherein the [electrolyte] battery contains no other sulfur or other sulfur species except for the linked sulfur species.

12. (Amended) The cathode material [of] according to claim 9, wherein the cathode material is a thiophene based polymer with the covalently linked sulfur species.

13. The cathode material [of] according to claim 9, wherein the conducting polymer [are] is covalently-derivatized with sulfides [and/]or sulfide-containing groups.

14. (Amended) A cathode material for use in a sulfur-based Lithium battery containing an electrolyte comprising, a sulfur species including sulfide components and a conducting polymer,

wherein the conducting polymer is a single component sulfur-based conducting polymer; and

wherein physical constraints of the conducting polymer and the sulfide components are provided via covalent bonds which are present regardless of charge state of the cathode material.

15. (Amended) An electric current producing cell comprising:

[a] an anode;

[b] a cathode [containing] containing a cathode material of claim 14; and[,]

[c] an electrolyte between the anode and cathode.

16. (Amended) An electric current producing cell comprising:

[a] an anode;

[b] a cathode [containing] containing a cathode material of claim 12; and[.]

[c] an electrolyte between the anode and cathode.

17. (Amended) An electric current producing cell comprising:

[a] an anode;

[b] a cathode [containing] containing a cathode material [selected by the method of claim 2]; and[,]

[c] an electrolyte between the anode and cathode[.];

wherein the cathode material includes a conduction polymer and a sulfur species which exhibit characteristics of: ionically conductive for Li<sup>+</sup> ions;

inherent charge capacity above 230 Ah/kg;  
substantial overlap of thermodynamic potentials of the  
sulfur species and the conducting polymer;  
electronic conductivity above  $10^{-4}$  S/cm of the cathode  
materials;  
no solubility in electrolyte solutions; and  
a capacity fade of less than 10% when the cathode  
material is cycled 100 times.

18. (Amended) The cathode material [of] according to claim 13, wherein the sulfur-derivatized conducting polymer is represented by a formula  $(R_i)_n(Y_jA_k)_{mL}$  [(where] wherein R is monomer or oligomer units of the conducting polymer, i is 1 to n and n is greater than 20, Y is a functionalizing group that provides additional physical or chemical properties to the conducting polymer and j is 0 to n; A is the sulfur species, k is 1 to n and m is 1 to 12.

19. (Amended) The cathode material [of] according to claim 18, wherein n is greater than 1000.

20. (Amended) The cathode material [of] according to claim 19, wherein n is greater than 100,000.

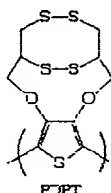
21. (Amended) The cathode material [of] according to claim 13, wherein the sulfur-derivatized conducting polymer represented by a formula  $(R)_n(YS_m)_{xL}$  [(where] wherein R is a conducting polymer backbone and n is greater than 20; Y is a functionalizing group; S is an organosulfur moiety, m is 1 to 12 and x is 1 to 4.

22. (Amended) The cathode material [of] according to claim 21, wherein n is greater than 1000.

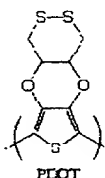
23. (Amended) The cathode material [of] according to claim 22, wherein n is greater than 100,000.

24. (Amended) The cathode material [of] according to claim 21, wherein R is polythiophene or [its] derivatives thereof.

25. (Amended) The cathode material [of] according to claim 24, wherein the single component sulfur-based conducting polymer is represented by:



26. (Amended) The cathode material [of] according to claim 24, wherein the single component sulfur-based conducting polymer is represented by:



**SINGLE COMPONENT SULFUR-BASED CATHODES FOR  
LITHIUM AND LITHIUM-ION BATTERIES**

**RELATED APPLICATIONS**

This application claims priority to U.S. Provisional patent application 60/118,068,  
the contents of which are incorporated herein by reference in their entirety.

**TECHNICAL FIELD**

The present invention relates generally to cathodes for rechargeable batteries. More particularly, the present invention relates to cathode materials based on conducting polymers and sulfur or selenide species and the method of selecting conducting polymers and sulfur or selenide species. The selection method accounts for characteristics of the conducting polymer and the sulfur or selenide species and the specific capacity, capacity fade, charge and discharge rate, physical and chemical stability, safety and other characteristics associated with battery cycles. More particularly, the present invention relates to a single component sulfur-based conducting polymer for use in lithium batteries and the synthesis of such material.

## BACKGROUND

Increasing reliance on sophisticated electronic technologies has exacerbated a need for reliable, portable sources of energy. The current worldwide market for rechargeable batteries exceeds \$4 billion. However, an estimated \$6 billion market in the United States alone remains untapped due to the inability of available products to meet the needs of a large industrial, consumer, and military based market. And the need is growing, particularly for high power applications such as electric vehicles and load-leveling equipment and weight or volume constrained applications such as portable computers, cellular phones, etc. Creative alternatives to current battery technologies must be developed.

Among available technologies, lithium and lithium-ion batteries represent the most promising technologies, especially in terms of their attractive energy densities when compared to nickel cadmium and nickel-metal hydride cells. This promise can be attributed in large part to the extremely high specific capacity available in theory from lithium (3862 A h/kg) and the reasonable charge capacity available from lithium-intercalated carbon (e.g. for  $\text{LiC}_6$ , 372 A h/kg) anodes.

However, realization of the full potential of that technology has been awaiting development of 1) electrolyte compositions able to withstand the high reactivities of those

anodes, and 2) inexpensive, stable cathodic materials also able to store high charge capacities. The present invention addresses resolution of the latter issue.

Batteries currently marketed utilize  $\text{LiCoO}_2$  cathodes, a material that has a theoretical specific capacity of 274 A h/kg and a practical specific capacity of 100 to 150 A h/kg. In realistic terms, then, cells using  $\text{LiCoO}_2$  can utilize only one-thirtieth of the potential energy per gram stored in lithium metal (or only one-third of the potential energy per gram stored in  $\text{LiC}_6$ ). While batteries based on such cathodes are suitable to meet short-term commercial needs, significant progress in this area must be based around developing cathodes with specific capacities similar to those of the best available anodes.

In terms of alternative cathode materials being currently studied, sulfur and sulfur-containing compounds offer the best opportunities in terms of high theoretical specific capacities. Sulfur cathodes operate by storing energy as disulfide bridges, a very stable oxidized material, then releasing it by reducing to thiolate moieties. This process is illustrated in Figure 1 for one material. While sulfur cathodes were the first employed for lithium laboratory cells, their use in practical batteries was abandoned primarily due to the insulating nature of those materials, which necessitates using high temperatures in order to facilitate mass transport within the cathodes.

However, advances in understanding and controlling electronic conductivity in composite materials has signaled a revival of that class of materials, as evidenced by ongoing exploratory or commercial efforts. Experimental lithium metal and lithium ion anode

prototypes of systems recently developed match or exceed current room temperature secondary battery performances in terms of gravimetric energy density (energy delivered per mass of the cathode material).

In U.S. Patent No. 5,789,108, Chu is pursuing technology based on cathodes composed of inorganic sulfur mixed with poly(ethylene oxide) (PEO), lithium salts, and carbon powders, while Skotheim et al., in U.S. Patent No. 5,529,860, are developing cathodes based on inorganic sulfur and poly(acetylene) derivatives. Those formulations represent attempts at achieving electronic and ionic access to the sulfur in those cathode *via* dispersion in an ionically conducting medium (PEO) which contains an electronic conductor (carbon)(Chu) or the use of a conducting polymer to effect both goals (Skotheim et al.).

Although such materials show excellent specific capacities during initial cycles, neither Chu nor Skotheim et al. have commercialized a sulfur or organosulfur based secondary battery due to high capacity loss, or "fade," observed for their cells over multiple charge and discharge cycles. Consideration of the possible origins of that behavior are obscured by a general lack of knowledge regarding the complicated electrochemistry of inorganic sulfur, compounded by the varying solubilities and chemical activities of the different forms of sulfur (e.g. polysulfide, oligosulfide, dimer, monomer ( $S^{2-}$ )), possible reaction between those species and the anode, and the likely growth of heterogeneous zones of non-conductive material that separate from the initial cathode mixture.



However, it is clear from recent work that the capacity fade observed is due in large part to diffusion of monomeric sulfur species out of the cathode. While interesting redox chemistry is typically evident in the first few cycles, it typically fades after several cycles to leave less desirable redox activity – viz. the organosulfur or sulfur or selenide component exits the cathode *via* dissolution into the electrolyte film, resulting in capacity loss during cycling.

In WO 99/03162, Skotheim et al., describe a polymer film that protects the lithium anode in a secondary battery. The film interferes to some degree with the reactions and thus reduces the overall efficiency of the battery. The film is needed when sulfur species are mobile and may migrate to the anode. Skotheim et al. do not suggest decreasing or eliminating the mobility of reactive sulfur species so that interference at the anode is decreased and thereby the efficiency of the battery is increased.

## Definitions

### Conducting polymer:

Conducting polymers are polymers through which electrons can move from one end of the polymer to the other. A conducting polymer transports voltage and/or current along its backbone or between its chains by changing the distribution of electrons in the polymer

chain. Such conduction typically occurs through conjugated  $\pi$  electronic functionalities, although some conducting polymers include other types of electronic functionalities. In some instances, conductivity occurs in short chains of the polymer ("oligomers"). In some cases, conductivity occurs in long chains of the polymer. Non-limiting examples of conducting polymers include poly(acetylene), poly(aniline), poly(pyrrole), poly(thiophene), poly(*p*-phenylene), (poly)phthalocyanine, etc. and derivatives thereof.

#### Redox species:

A redox species is an atom, molecule, or macromolecule that accepts or releases one or more electrons when placed under an electric field of appropriate direction and magnitude. Non-limiting examples of redox species include ruthenium hexamine chloride, ferrocene, gold, poly(pyrrole), hexanethiol, and similar species and derivatives.

#### Battery:

A battery is comprised of one or more cells each comprised of an electropositive anode such as lithium or nickel, an electronegative cathode such as metal oxide, sulfur, or cadmium, and an ionically-conducting separator, such as poly(ethylene oxide), propylene carbonate, or Nafion, that contain an electrolytic salt such as lithium hexafluorophosphate, sodium chloride, etc. A cell "discharges" by allowing electrons to pass via an external circuit

from a higher energy state in the anode to a lower energy state in the cathode while allowing ions to pass through the separator. In lithium-based cells, Li ions pass from the anode through the separator to the cathode. The electrons that pass through the external circuit may be used to perform work. In a rechargeable battery, this electron and ion movement may be reversed to some extent by applying an external current to the cell to "charge" the cell. The typical forms of batteries, and more specifically of lithium-based batteries are well known to those skilled in the art.

#### Sulfur species:

In this document, sulfur species include atoms, molecules, and macromolecules that contain at least one sulfur atom. Typical terms used to describe such molecules include organosulfur, sulfur, sulfide, disulfide, thio, thiol, thiolate, mercapto, mercaptan, etc. In some cases, the sulfur species contains a negatively-charged or proton-associated sulfur atom that is covalently bound to another atom through a single bond. This type of sulfur species is capable of releasing an associated cation or proton and forming a disulfide bond with a similar atom. In other cases, the sulfur species contains sulfur atoms that are multiply bound to other atom or atoms and are not capable of forming disulfide bonds. In all cases, in this document, sulfur species refers to atoms, molecules, and macromolecules that contain at least one sulfur atom that can act in part or in whole as a redox species.

### Selenium species

In this document, selenium species include atoms, molecules, and macromolecules that contain at least one selenium atom. Typical terms used to describe such molecules include selenide, selenate, diselenides, etc. In some cases, the selenide species contains a negatively-charged or proton-associated selenide atom that is covalently bound to another atom through a single bond. This type of selenide species is capable of releasing an associated cation or proton and forming a diselenide bond with a similar atom. In other cases, the selenide species contains selenide atoms that are multiply bound to other atom or atoms and are not capable of forming diselenide bonds. In all cases, in this document, selenide species refers to atoms, molecules, and macromolecules that contain at least one selenide atom that can act in part or in whole as a redox species.

### SUMMARY OF INVENTION

One aspect of the present invention pertains to the selection of cathode materials. The cathode materials of concern are the conducting polymer or backbone and the redox active species or sulfur species. The selection of the materials is based on the characteristics of the materials relating to the other components of the batteries and to each other.

In one embodiment, the selection of cathode materials is based on one or more of the following characteristics of the conducting polymer and/or the sulfur or selenide species: ease of fabrication using straightforward synthetic procedures; ionically conductive for  $\text{Li}^+$  ions; no labile protons in the material; a high density of electroactive species per weight and volume (i.e. large inherent charge capacity); good overlap of the thermodynamic redox potentials of the electroactive substituents and the conducting polymer backbone; reasonable electronic conductivity of the composite; no solubility in typical electrolyte solutions; and electrochemically, physically, and chemically stable to many repeated charge and discharge cycles. In a preferred embodiment, the selection of the cathode materials is based on all of the above identified characteristics for both the conducting polymer and the sulfur or selenide species.

In one embodiment, the selection of cathode materials is based on the overlap of the thermodynamic potentials of the electroactive substituents of the sulfur species and the conducting polymer. The cathode materials are chosen based on the redox mediation window. The conducting polymer mediates electrons between the current collector and the sulfur or selenium species. Conducting polymers exhibit potential-dependent conductivities. When the potential is in the "double-layer" region of the conducting polymer (that is, when the conducting polymer is releasing or accepting electrons), the conductivity of the polymer is much higher than when the potential is more negative or more positive of that region. If the conducting polymer is inherently in a less-conductive state in the potential region where the sulfur or selenium species exhibits redox species behavior, mediation of electrons

between the current collector and the sulfur or selenium species is poorly effected, the material is less desirable, and the battery performance is poorer.

In a preferred embodiment, the resulting premise of the selection process of materials is that the redox active species or sulfur species that are mobile are not compatible with long-life, high-capacity batteries.

Another aspect of the present invention pertains to resultant cathode materials identified by the use of the selection process identified above.

In a preferred embodiment, the cathode materials were selected because they exhibit overlap of the thermodynamic potentials of the electroactive substituents of the sulfur species and the conducting polymer. The cathode materials form a redox mediation window. The conducting polymer mediates electrons between electrode(s) and the sulfur species in an effective fashion.

In a preferred embodiment, the sulfur species is NOT covalently linked to the conducting polymer backbone. An example of this system is that comprising a mixture of poly(3,4-ethylenedioxythiophene) (PEDT) and 2,5-dimercapto-1,3,4-thiadiazole, dilithium salt ( $\text{Li}_2\text{DMcT}$ ). PEDT is available as an aqueous dispersion.  $\text{Li}_2\text{DMcT}$  is dissolved directly into the PEDT dispersion at high concentrations. Properly treated films cast from that mixture are used as cathode materials in lithium and lithium-ion cells. Alternately, films are

prepared by electrochemical or chemical oxidation of the PEDT monomer and  $\text{Li}_2\text{DMcT}$  from the same or different solutions in a homogeneous or layered arrangement.  $\text{Li}_2\text{DMcT}$  contains no labile protons, so its use in the cathode is attractive. PEDT has a wide potential window of conductivity, contains no labile protons, and is not proton-doped, so its use in the cathode is attractive.

One embodiment of the present invention is the cathode materials are not mobile. Specifically, the redox active species or sulfur species is not mobile. The redox active species is bound to the conducting polymer and is not able to migrate from the conducting polymer.

In a preferred embodiment, the cathode material is a single component sulfur-based conducting polymer with the sulfur species covalently linked to the conducting polymer. The link of the sulfur species and the conducting polymer provides suitable fade characteristics by not allowing the sulfur species to be soluble in the electrolyte. In this preferred embodiment, sulfur or other sulfur species apart from the covalently linked sulfur species may or may not be present. Most preferably the cathode material contains no other sulfur or sulfur species apart from the bound sulfur species.

In a preferred embodiment, the cathode material is a thiophene based polymer with covalently linked sulfur species. Such conducting polymers have been covalently-derivatized with sulfides and/or sulfide-containing groups and employed as battery cathode materials. Physical constraints of the conducting polymer and sulfide components via covalent bonds

which are present regardless of charge state of the cathode represents a novel step in the field.

Yet another aspect of the present invention pertains to a method of synthesis of the selected cathode material.

Still another aspect of the present invention pertains to batteries which comprise an anode: cathode material(s) of the present invention, as described herein; and a separator between the anode and the cathode materials

## BRIEF DESCRIPTION OF DRAWINGS

Fig. 1 shows a sulfur cathode in operation by storing energy as a disulfide bridge then releasing it by reducing to thiolate moieties.

Fig. 2 shows an example of an inappropriate overlap of thermodynamic potentials between polyaniline and an organosulfur.

Fig. 3 shows a general formula of a conducting polymer of the present invention.

Fig. 4 shows a more specific formula of the present invention.



Fig. 5 shows the substituent parts of the polythiophene conducting polymer.

Fig. 6 shows two resultant conducting polymers of the present invention.

## DETAILED DESCRIPTION OF INVENTION

One aspect of the present invention pertains to the selection of cathode materials. The cathode materials of concern are the conducting polymer or backbone and the redox active species or sulfur species. The selection of the materials is based on the characteristics of the materials relating to the other components of the batteries and to each other.

In one embodiment, the selection of cathode materials is based on one or more of the following characteristics of the conducting polymer and/or the sulfur species: ease of fabrication using straightforward synthetic procedures; ionically conductive for  $\text{Li}^+$  ions; no labile protons in the material; a high density of electroactive species per weight and volume; good overlap of the thermodynamic potentials of the electroactive substituents and conducting polymer backbone; reasonable electronic conductivity of the composite; no solubility in typical electrolyte solutions; and electrochemically stable to many repeated charge and discharge cycles. In a preferred embodiment, the selection of the cathode materials is based on all of the above identified characteristics for both the conducting polymer and the sulfur species.

*Molecular design of innovative sulfur-based cathode materials*

The chemical and physical constraints imposed on cathode materials are substantial. The specific properties required include ease of fabrication using straightforward synthetic procedures.

In sulfur-based batteries, the sulfur species and preferably the conducting polymer must be ionically conductive for  $\text{Li}^+$  ions. The chemistry of sulfur-based batteries necessitates the requirement of the cathode materials to be ionically conductive for  $\text{Li}^+$  ions.

A material that contains mobile redox species presents stability, capacity fade, and safety problems when used as a cathode material in a lithium or lithium-ion or lithium polymer cell. For example, 2,5-dimercapto-1,3,4-thiadiazole contains two labile protons. Use of that material as a component of a cathode material leads to transport of the labile protons via intermediate species into the electrolyte and eventually to the anode, where spontaneous electrochemical reduction by the anode creates hydrogen gas. Similar events can occur when poly(aniline), a proton-doped conducting polymer, is used as a component of a cathode material. This constraint includes the selection of conducting polymers and sulfur species that do not contain labile protons at any stage of the battery reaction.

A battery's effectiveness is attributable to the charge capacity. Selecting a sulfur species and conducting polymer with a high density of electroactive species per weight and volume (i.e. large inherent charge capacity) increases the effectiveness of the cathode and battery overall.

A battery's effectiveness is also dependent on the electronic conductivity of the cathode materials. Selecting a sulfur species and conducting polymer with an electronic conductivity above  $10^{-6}$  S/cm, more preferably above  $10^{-5}$  S/cm, more preferably above  $10^{-4}$  S/cm, more preferably above  $10^{-3}$  S/cm, and most preferably above  $10^{-2}$  S/cm increases a battery's effectiveness.

The solubility of the sulfur species or conducting polymer in the electrolyte inhibits the efficiency of the battery. When sulfur species or other electroactive species associated with the conducting polymer are mobile in the electrolyte, the species may migrate towards the anode and a decrease in efficiency results when the species contact the anode. Over time the anode increasingly becomes contacted with species and a loss of electroactive sites may be seen on the anode. The solubility of the sulfur species also leads to collection of the active sulfur away from the conducting polymer and therefore a loss of redox species in the cathode. Thus, selecting sulfur species and conducting polymers which are not soluble in the electrolyte solution increases the efficiency of the battery and reduces the fade and poor cyclability typical of sulfur-based batteries.

The current sulfur-based batteries in use exhibit considerable fade over even 100 cycles. Many factors contribute to the fade observed in conventional sulfur-based batteries. However, by selecting the conducting polymer and sulfur species of the cathode materials that are electrochemically stable to many repeated charge and discharge cycles the fade is reduced.

Unfortunately, previous sulfur-based cathodes have not satisfied most of these requirements. However, understanding the structure-function relationships for these materials allows sufficient tailoring of their properties to increase their effectiveness in rechargeable batteries.

### ***Redox Mediation Window***

In one embodiment, the selection of cathode materials is based on the overlap of the thermodynamic potentials of the electroactive substituents of the sulfur species and the conducting polymer. The cathode materials are chosen based on the redox mediation window. The conducting polymer mediates electrons between electrode and sulfur species.

An example of *inappropriate* overlap of thermodynamic potentials, the redox response of composite cathode components are shown in Figure 3. While oxidation of the organosulfur occurs when the polyaniline is primarily in its metallic state (indicated by a dashed line at 3.1 V), reduction of the resulting disulfide occurs in a potential window where

the polyaniline is primarily in its insulating state (indicated by a dashed line at 2.6 V). The practical consequences of that thermodynamic mismatch between components is apparent in devices using such cathodes – charging of the cells occurs quickly, but discharging is slow and typically incomplete.

### ***Cathode Materials***

Another aspect of the present invention pertains to resultant cathode materials identified by the use of the selection process of the present invention.

In a preferred embodiment, the cathode materials were selected because they exhibit overlap of the thermodynamic potentials of the electroactive substituents of the sulfur species and the conducting polymer. The cathode materials form a redox mediation window. The conducting polymer mediates electrons between electrode(s) and the sulfur species.

In a preferred embodiment, the resulting premise of the selection process of materials is the redox active species or sulfur species that are mobile are not compatible with long-life, high-capacity batteries. The sulfur species in the cathode materials is not mobile and is not soluble in the electrolyte of the battery and does not include labile protons that are mobile or soluble in the electrolyte. More preferentially, the cathode materials are not mobile. Specifically, the redox active species or sulfur species is not mobile. The redox active species is bound to the conducting polymer and is not able to migrate from the conducting polymer.

In a preferred embodiment, the cathode material is a single component sulfur-based conducting polymer with the sulfur species covalently linked to the conducting polymer. The link of the sulfur species and the conducting polymer provides suitable fade characteristics by not allowing the sulfur species to be soluble in the electrolyte. In this preferred embodiment, sulfur or other sulfur species in the cathode apart from the covalently linked sulfur species may or may not be present. Most preferably the cathode material contains no other sulfur or sulfur species apart from the bound sulfur species.

In a preferred embodiment, the cathode material is a thiophene based polymer (such as polythiophene) with covalently linked sulfur species. Such conducting polymers have been covalently-derivatized with sulfides and/or sulfide-containing groups as battery cathode materials. Physical constraints of the conducting polymer and sulfide components via covalent bonds which are present regardless of charge state of the cathode represents a novel step in the field.

Using the method of the present invention a resultant cathode material was identified. Sulfur-derivatized conducting polymers based on the oxide-substituted poly(thiophene) backbone are synthesized. Those polymers show good thermodynamic overlap with sulfide oxidation and reduction (*i.e.* charge and discharge). Covalent linkage of the sulfur groups to the backbone provides molecular-level ordering of the material, effecting homogeneous conductivity, cycling stability, and physical structure of the cathode.

In one embodiment, the sulfur-derivatized conducting polymers have the general formula  $(R_i)_n(Y_jA_k)_m$  where R is monomer or oligomer units of a conducting polymer, i is 1 to n and n is greater than 20, more preferably greater than 100, more preferably greater than 1000, more preferably greater than 10,000 and most preferably greater than 100,000; Y is a functionalizing group that provides additional physical or chemical properties to the conducting polymer and j is 0 to n; A is a sulfur species, k is 1 to n and m is 1 to 12. A simplified representation of the general formula is shown in figure 3.

More particularly, the sulfur-derivatized conducting polymers have the general formula  $(R)_n(YS_m)_x$  where R is a conducting polymer backbone and n is greater than 20, more preferably greater than 100, more preferably greater than 1000, more preferably greater than 10,000 and most preferably greater than 100,000; Y is a functionalizing group; S is an organosulfur moiety, m is 1 to 12 and x is 1 to 4. In a preferred embodiment, R is polythiophene or its derivatives. The formula is shown in figure 4. The preferred embodiment is shown in figure 5 based on the polythiophene backbone  $R_n$ .

Specifically, the present invention also concerns covalently derivatizing an electronically conducting polymer with a high density of electroactive sulfur species. The materials operate near the high oxidation potentials exhibited by the more common metal oxide cathodes but show far better ionic conductivity. This is accomplished by applying pre-existing, high yield organic synthesis procedures to the formation of monomeric, and then polymeric species composed of thiophene-based polymer chains with thiolate substituents. The synthesis steps are geared toward forming a reasonably high molecular weight polymer

while at the same time incorporating a high density of electroactive species that are not only electrochemically stable, but also protect the polymer from chemical degradation.

Another aspect of the present invention pertains to a method of designing conducting polymers covalently-derivatized with sulfur species such that the chemical, physical, and electrochemical properties of the designed material are advantageous to use in a rechargeable cell. For example, for the conducting polymers represented by Figure 6, the number of carbon atoms between the oxygen atoms and the sulfide-containing six-membered ring are varied to affect both the proximity of the sulfide-containing six-membered ring to the conducting polymer backbone and the flexibility of the attachment of the sulfide-containing six-membered ring. Likewise, other atom or functional groups such as sulfur, selenium, amides, amines, etc. are substituted for the oxygen atoms in order to affect the conductivity and relative energy of the conducting polymer backbone. Furthermore, the number of carbon atoms in the sulfide-containing six-membered ring are reduced or increased in order to affect the electronic, physical, or chemical properties of the sulfur atoms. For instance, reducing the number of carbon atoms to produce a sulfide-containing four-membered ring causes additional strain on the disulfide oxidation product and results in higher potentials for redox activity of that sulfur species. Finally, additional substituents are placed on the conducting polymer ring, functionalizing group, or sulfur species in order to affect the chemical and physical properties of the material. For instance, attaching a alkylsulfonate at the carbon atom above the oxygen atom increases the solubility and miscibility of the material.



Yet another aspect of the present invention pertains to a method of synthesis of the selected cathode material.

Still another aspect of the present invention pertains to batteries which comprise an anode; cathode material(s) of the present invention, as described herein; and a separator between the anode and the cathode materials. A battery with the cathode material as sulfur-derivatized conducting polymers based on the oxide-substituted poly(thiophene) backbone are used as a substitute cathode in existing lithium, lithium-ion, and lithium polymer rechargeable batteries.

### ***Synthesis of Sulfur-Derivatized Cathode Materials.***

#### **Thiophene based cathode materials**

Two thiophene-based polymers, structures shown in Figure 6, were synthesized. The first (PDDT) follows a tractable route to produce a material with an attractive theoretical specific capacity (235 A h/kg). Synthesis of the second polymer (PDPT) was more uncertain due to its bulky substituents, yet its synthesis yielded a material with a very attractive theoretical specific capacity (332 A h/kg).

PDDT was chosen as a cathode material in part because a stable 6-member ring is formed during oxidation to the disulfide.

PDPT, shown in Figure 6, offers higher specific capacity because of the increased number of disulfide substituents

*Development of deposition techniques for the polymers synthesized*

Processing of conducting polymers is a non-trivial issue – the very traits that make those materials conductive also result in low solubility of the polymers in most solvent systems. That problem is compounded for the systems described herein by the typically poor solubility of sulfide species.

For a preferred embodiment, if a particular polymer exhibits some solubility in a given, non-protic solvent such as N-methylpyrrolidinone or methylene chloride, then a saturated solution is directly cast onto the current collector. Care was taken to generate uniformly small particle sizes of the polymer prior to deposition. Evaporation of the solvent under normal drying conditions leads to a relatively adherent film due to the soluble phase acting as a binder. If a quality film is generated, but adhesion to the current collector is poor, then the current collector is chemically or mechanically treated prior to film deposition.

For another embodiment, mechanical or high pressure or temperature methods are employed to prepare suitable films of the cathode material. For example, extrusion, heat-pressing, and other methods are available.

In a preferred embodiment, the derivatized conducting polymer is prepared by chemical or electrochemical oxidation of its monomer in the presence of a suitable current collector. For example, the monomer of PDDT (Figure 6) is electrochemically oxidized at a stainless steel electrode by applying a potential of more than one volt versus the Ag/AgCl reference redox couple. This application results in the preparation of a film of PDDT on the stainless steel suitable for use as a cathode material.

If a particular polymer is not sufficiently soluble in any appropriate solvent system, and if the mechanical preparation of reasonable films is not possible, carbon paste electrodes containing the polymers are prepared in order to allow electrochemical testing of their properties.

**Example 1**

The first attempted, unsuccessful, synthesis involved Cu(I) assisted nucleophilic displacement of the bromine groups of 3,4-dibromothiophene with 1,2-dithiane-4,5-diol to form the desired cyclic ester (Scheme 1).

**Experimental:**

**3,4-(1,2-dithiane-4,5-diol) Thiophene.** Pyridine (5 mL) was added to 1,2-dithiane-4,5-diol (0.27 g, 1.80 mmol), CuI (0.01 g, 0.07 mmol) and KO<sup>t</sup>Bu (0.06 g, 0.54 mmol) to produce a yellow solution which turned green after stirring at ambient temperature over a period of 1h. 3,4-dibromothiophene (0.09 g, 0.36 mmol) was then added to the reaction mixture which was heated at 100 °C for 24h. A distillation was then done to remove pyridine. The remaining solution was dissolved in 0.05 M EDTA to remove complexed copper. An extraction was done with ethyl acetate. The organic, ethyl acetate, layer was concentrated under vacuum. This procedure did NOT result in the desired compound, the actual identity of the remaining solution was not confirmed.

At this point a new synthetic procedure was devised (Scheme 2) utilizing 3,4-dihydroxythiophene. 3,4-dihydroxythiophene can be synthesized by adding 2,2'-thiobisacetate ethyl ester to diethyl oxalate in a solution of ethanol and sodium metal, according to the method of Hinsberg, to produce 3,4-dihydroxy-2,5-dicarbethoxythiophene, compound A in Scheme 3. Hydrolysis of compound A with ethanolic sodium hydroxide results in a dicarboxylic acid, compound B. Heating compound B under a reduced atmosphere causes sublimation of compound C as a yellow

powder. Care must be taken in isolation because compound C decomposes readily on exposure to heat, light and moisture. Alternatively, a more direct approach toward the formation of 3,4-dihydroxythiophene is to add  $\text{HS}^-$  and a base, or simply  $\text{S}^{2-}$ , to 1,4-dibromo-2,3-butanedione. Once 3,4-dihydroxythiophene was obtained it was reacted with 2 equivalents of ethyl bromoacetate under basic conditions to form compound D which when treated with 2 equivalents of LDA in the presence of  $\text{I}_2$  or another oxidizing agent formed compound F. Alternatively, compound F can be synthesized by adding 3,4-dihydroxythiophene to a cyclic sulfate ethyl ester, compound E, in the presence of potassium tert-butoxide at elevated temperatures. Upon reduction of F with  $\text{LiAlH}_4$  compound G was formed. Treatment of G with  $\text{PBr}_3$  resulted in the formation of compound H. Conversion of compound H to the desired monomer, I, is accomplished by treatment with potassium thioacetate followed by acidification under aqueous conditions, then  $\text{I}_2$  addition to result in the desired monomeric compound I. Alternatively, treatment of compound H with 2 equivalents of ammonium thiocyanate under acidic conditions in the presence of an oxidizing agent,  $\text{I}_2$ , also resulted in formation of compound I. The same compound I was also formed by adding 2 equivalents of  $\text{HS}^-$  and an oxidizing agent to compound H. Polymerization of compound I was accomplished in the presence of  $\text{FeCl}_3$ .

#### Experimental:

**2,2'-thiobisacetate ethyl ester.**  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  (14g, 58 mmol) was dissolved in an  $\text{EtOH}/\text{H}_2\text{O}$  (60 mL/36 mL) solution. Ethyl bromoacetate was added. This was heated at 80 °C for 19 h under  $\text{N}_2$  with an oil bath. Upon cooling to ambient temperature  $\text{EtOH}$

was removed *in vacuo* leaving a turbid aqueous solution. Washed with Et<sub>2</sub>O (2 x 40 mL), dried the Et<sub>2</sub>O layer with MgSO<sub>4</sub>. The Et<sub>2</sub>O was evaporated under vacuum and the remaining solution was distilled to yield 4.66 g (39%) of a yellow oil. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz, 23 °C): δ 3.87 (q, 2H; OCH<sub>2</sub>CH<sub>3</sub>), 3.15 (s, 2H; SCH<sub>2</sub>), 0.90 (t, 3H, OCH<sub>2</sub>CH<sub>3</sub>).

**2,5-dicarbethoxy-3,4-dihydroxythiophene.** Diethyl oxalate (6.58 g, 45 mmol) was added to 2,2' thiobisacetate ethyl ester (4.66 g, 23 mmol) to produce a yellow-orange solution. A solution of Na (1.56 g, 68 mmol) in EtOH (24 mL) was added to produce a white/yellow precipitate, this was mixed well for 10 minutes. H<sub>2</sub>O (50 mL) was added to the reaction mass with cooling in an ice bath. Concentrated HCl was added dropwise until acidified. This was allowed to stand in the refrigerator for 12 days. At this point a cold filtration was done to isolate a white solid.

**2,5-dicarboxy-3,4-dihydroxythiophene.** EtOH (30 mL) was added to 2,5-dicarbethoxy-3,4-dihydroxythiophene (1 g). A solution of NaOH (4.0 g) in H<sub>2</sub>O (20 mL) was added and refluxed under N<sub>2</sub> for 20 h. Upon cooling to ambient temperature the EtOH was removed by distillation and the residue was redissolved in H<sub>2</sub>O then acidified with 15 % HCl(aq) when a white ppt was obtained. This product was collected by filtration and washed with cold H<sub>2</sub>O then crystallized from dilute MeOH to give colorless needles.

**3,4-dihydroxythiophene.** The acid, 2,5-dicarboxy-3,4-dihydroxythiophene (1g), was sublimed in a sublimation tube at 120 °C/3mm. The yellowish decarboxylated product was resublimed and then crystallized from benzene and ligroin to give pale yellow needles.

**Cyclic sulfate ethyl ester.** Carbon tetrachloride (25 mL) was added to diethyl-L-tartrate (4.3 mL, 25 mmol). Thionyl chloride (3.57 g, 30 mmol) was added via syringe slowly and the solution was refluxed for 50 min. then cooled in an ice bath and diluted with CH<sub>3</sub>CN (25 mL). RuCl<sub>3</sub>·3H<sub>2</sub>O (8 mg, 0.03 mmol) and H<sub>2</sub>O (38 mL) were added. followed by NaIO<sub>4</sub> (16 g, 75 mmol). The mixture was stirred at room temperature for 17 h. The mixture was then diluted with 200 mL Et<sub>2</sub>O and the two phases were separated. The organic layer was washed with H<sub>2</sub>O (10 mL), saturated NaHCO<sub>3</sub> (2 x 20 mL), and brine (10 mL). After drying over MgSO<sub>4</sub>, the solution was filtered through a small pad of silica gel. The filtrate was then concentrated to yield analytically pure colorless crystals.

### Example 2

The use of 3,4-dihydroxythiophene is also necessary in the synthesis of the second desired monomeric component shown in figure 2 and will be synthesized as described above. Scheme 4 shows the mechanism of formation of the compound shown in figure 2. The reaction of 3,4-dihydroxythiophene with 2,2-dimethyl-1,3-dioxolane-4-methanol in the presence of a base, followed by H<sub>3</sub>O<sup>+</sup> addition, resulted in the formation of compound K. Alternatively, this is also formed by the addition of 2 equivalents of allyl bromide to 3,4-dihydroxythiophene in the presence of a base. The resulting product, J, was treated with catalytic amounts of OsO<sub>4</sub> and sodium periodate to produce compound K. Once compound K was obtained it was treated with PBr<sub>3</sub> or tosyl chloride to form L, where LG = Br or OTs. Compound L can also be produced by the addition of 1,2,3-tribromopropane to 3,4-dihydroxythiophene. Treatment of L with potassium thioacetate

resulted in formation of M. Polymerization of this material was done in the cathode assembly step followed by removal the thioacetate protecting groups during curing of the cathode, through the use of lithium hydroxide. Alternatively, compound N can be reached directly by treating compound L with HS<sup>-</sup> and an oxidizing agent. At this point polymerization of N was accomplished electrochemically.

#### Experimental:

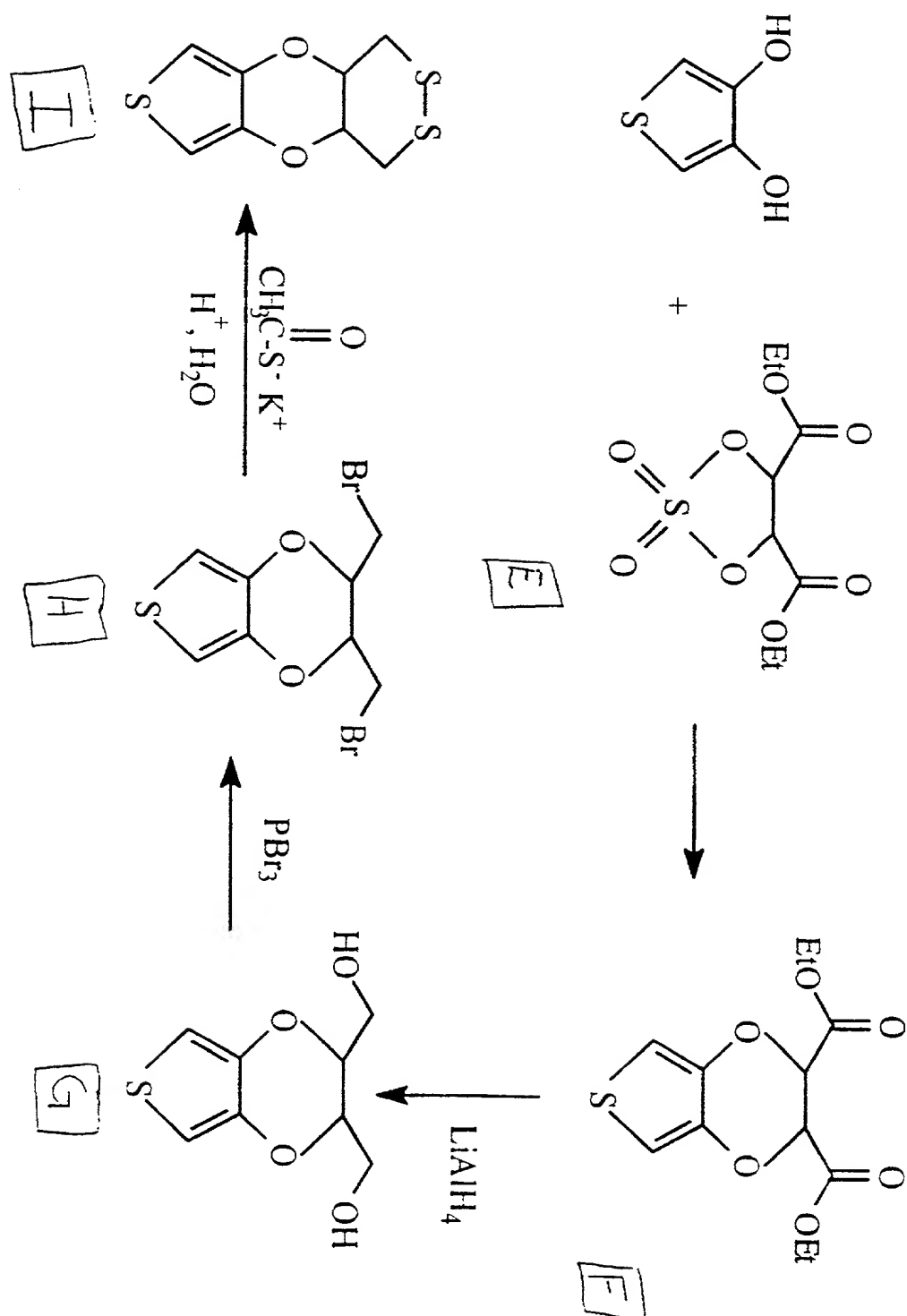
**2,2'-thiobisacetate ethyl ester.** Na<sub>2</sub>S·9H<sub>2</sub>O (14g, 58 mmol) was dissolved in an EtOH/H<sub>2</sub>O (60 mL/36 mL) solution. Ethyl bromoacetate was added. This was heated at 80 °C for 19 h under N<sub>2</sub> with an oil bath. Upon cooling to ambient temperature EtOH was removed *in vacuo* leaving a turbid aqueous solution. Washed with Et<sub>2</sub>O (2 x 40 mL), dried the Et<sub>2</sub>O layer with MgSO<sub>4</sub>. The Et<sub>2</sub>O was evaporated under vacuum and the remaining solution was distilled to yield 4.66 g (39%) of a yellow oil. <sup>1</sup>H NMR (C<sub>6</sub>d<sub>6</sub>, 400 MHz, 23 °C): δ 3.87 (q, 2H; OCH<sub>2</sub>CH<sub>3</sub>), 3.15 (s, 2H; SCH<sub>2</sub>), 0.90 (t, 3H, OCH<sub>2</sub>CH<sub>3</sub>).

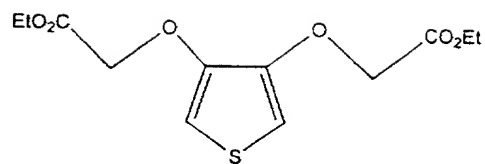
**2,5-dicarbethoxy-3,4-dihydroxythiophene.** Diethyl oxalate (6.58 g, 45 mmol) was added to 2,2' thiobisacetate ethyl ester (4.66 g, 23 mmol) to produce a yellow-orange solution. A solution of Na (1.56 g, 68 mmol) in EtOH (24 mL) was added to produce a white/yellow precipitate, this was mixed well for 10 minutes. H<sub>2</sub>O (50 mL) was added to the reaction mass with cooling in an ice bath. Concentrated HCl was added dropwise until acidified. This was allowed to stand in the refrigerator for 12 days. At this point a cold filtration was done to isolate a white solid.

**2,5-dicarboxy-3,4-dihydroxythiophene.** EtOH (30 mL) was added to 2,5-dicarbethoxy-3,4-dihydroxythiophene (1 g). A solution of NaOH (4.0 g) in H<sub>2</sub>O (20 mL) was added



Scheme 2

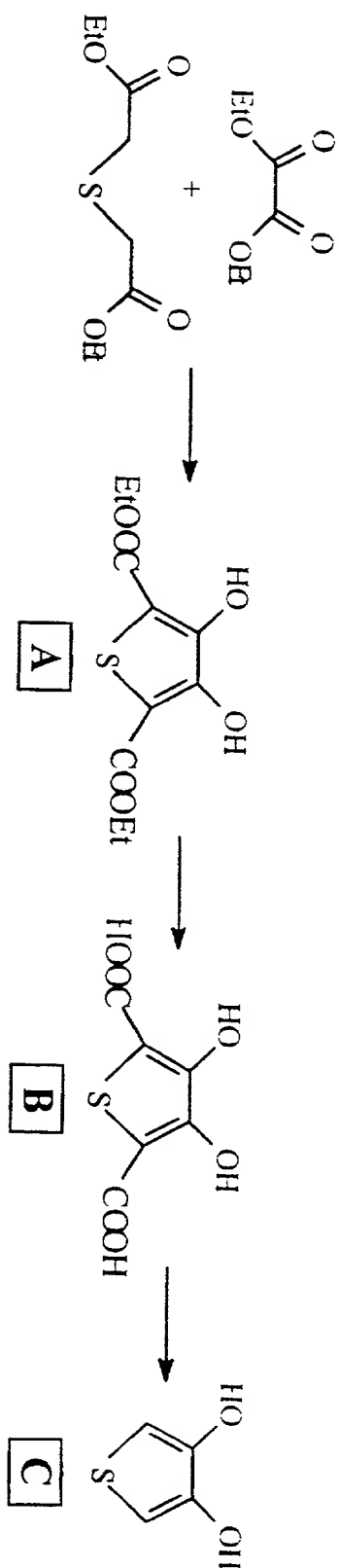




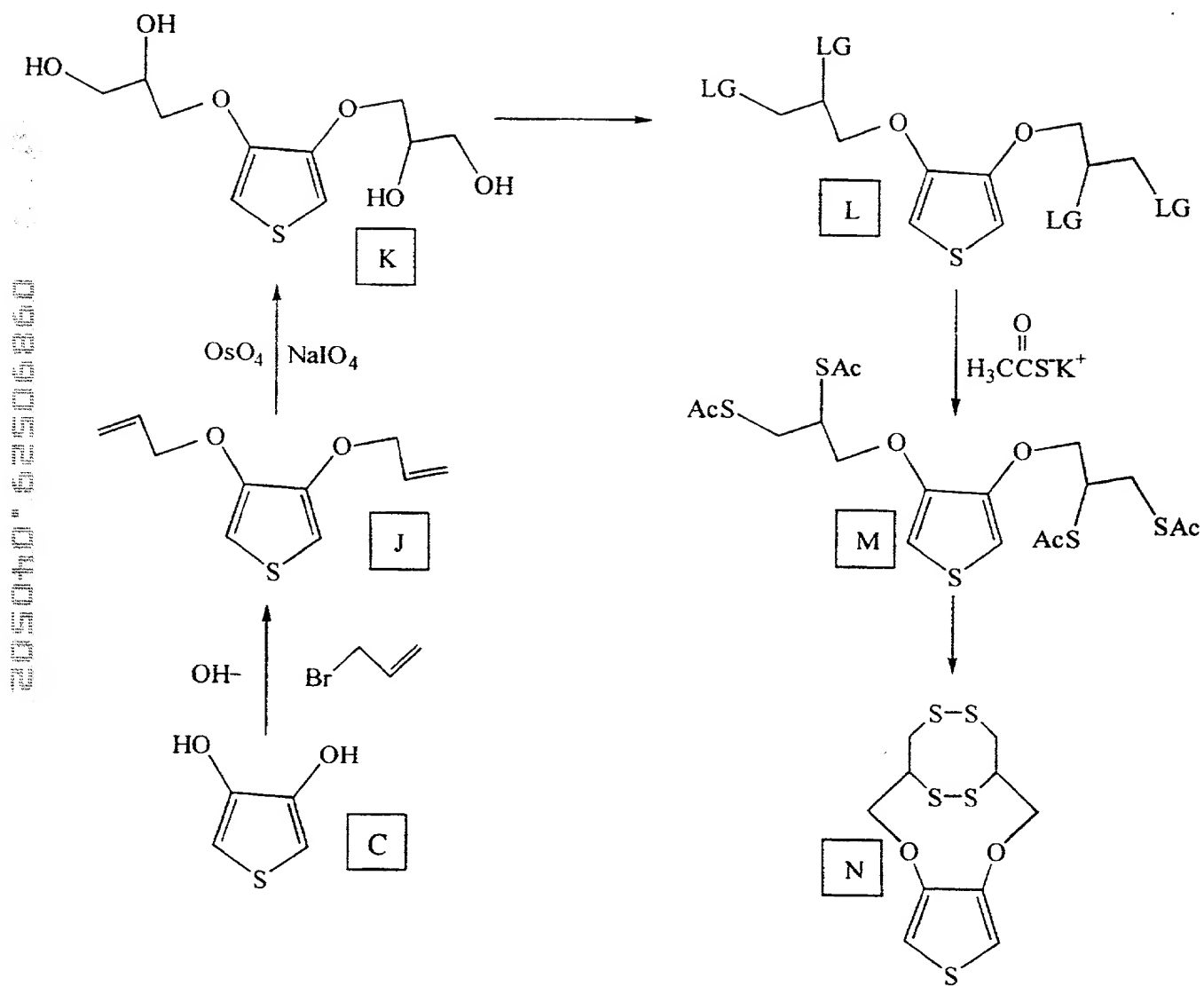
D

62506860

Scheme 3.



## Scheme 4



and refluxed under N<sub>2</sub> for 20 h. Upon cooling to ambient temperature the EtOH was removed by distillation and the residue was redissolved in H<sub>2</sub>O then acidified with 15 % HCl(aq) when a white precipitate was obtained. This product was collected by filtration and washed with cold H<sub>2</sub>O then crystallized from dilute MeOH to give colorless needles.

**3,4-dihydroxythiophene.** The acid, 2,5-dicarboxy-3,4-dihydroxythiophene (1g), was sublimed in a sublimation tube at 120 °C/3mm. The yellowish decarboxylated product was resublimed and then crystallized from benzene and ligroin to give pale yellow needles.

205040" 52506860

### CLAIMS

1) A method of selecting cathode materials for a sulfur-based Lithium battery wherein the cathode comprises a conducting polymer and a sulfur species;

identifying a characteristic of the conducting polymer;

identifying a characteristic of the sulfur species;

evaluating the characteristic of the conducting polymer and the sulfur species;

selecting the conducting polymer and the sulfur species based on the identified characteristic;

wherein the identified characteristic of the sulfur species and the identified characteristic of the conducting polymer are at least one characteristic selected from the group consisting of: ease of fabrication using straightforward synthetic procedures; ionically conductive for  $\text{Li}^+$  ions; a high density of electroactive species per weight and volume/large inherent charge capacity  $> 230 \text{ Ah/kg}$ ; good overlap of thermodynamic potentials of the sulfur species and the conducting polymer; reasonable electronic conductivity ( $10^{-4} \text{ S/cm}$ ) of the cathode materials; no solubility in electrolyte solutions; or electrochemically stable to many repeated charge and discharge cycles/a capacity fade of less than 10% when the cathode material is cycled 1000 times.

2) The method of claim 1 wherein the identified characteristics are all of the at least one characteristics.

3) The method of claim 1 wherein the at least one characteristic is good overlap of thermodynamic potentials of the sulfur species and the conducting polymer.

4) The method of claim 1 wherein the at least one characteristic is no solubility in electrolyte solutions.

5) A cathode material for use in a sulfur-based Lithium battery comprising a sulfur species and a conducting polymer;

wherein the conducting polymer and the sulfur species exhibit at least one characteristic selected from the group consisting of: ease of fabrication using straightforward synthetic procedures; ionically conductive for  $\text{Li}^+$  ions; a high density of electroactive species per weight and volume/large inherent charge capacity  $> 230 \text{ Ah/kg}$ ; good overlap of thermodynamic potentials of the sulfur species and the conducting polymer; reasonable electronic conductivity ( $10^{-4} \text{ S/cm}$ ) of the cathode materials; no solubility in electrolyte solutions; or electrochemically stable to many repeated charge and discharge cycles/a capacity fade of less than 10% when the cathode material is cycled 1000 times.

6) The cathode material of claim 5, wherein the at least one characteristic includes all of the characteristics from the group consisting of: ease of fabrication using straightforward synthetic procedures; ionically conductive for  $\text{Li}^+$  ions; a high density of electroactive species per weight and volume/large inherent charge capacity  $> 230 \text{ Ah/kg}$ ; good overlap of thermodynamic potentials of the sulfur species and the conducting polymer;

reasonable electronic conductivity ( $10^{-4}$  S/cm) of the cathode materials: no solubility in electrolyte solutions: or electrochemically stable to many repeated charge and discharge cycles/a capacity fade of less than 10% when the cathode material is cycled 1000 times.

7) The cathode material of claim 5, wherein the at least one characteristic is good overlap of thermodynamic potentials of the sulfur species and the conducting polymer.

8) The cathode material of claim 5, wherein the at least one characteristic is good overlap of thermodynamic potentials of the sulfur species and the conducting polymer and no solubility in electrolyte solutions.

9) A cathode material for use in a sulfur-based Lithium battery containing an electrolyte comprising, a sulfur species and a conducting polymer wherein the conducting polymer is a single component sulfur-based conducting polymer with the sulfur species covalently linked to the conducting polymer.

10) The cathode material of claim 9, wherein the covalent link of the sulfur species and the conducting polymer provides suitable fade characteristics by not allowing the sulfur species to be soluble in the electrolyte.

11) The cathode material of claim 9, wherein the electrolyte contains no other sulfur or other sulfur species except for the linked sulfur species.



12) The cathode material of claim 9, wherein the cathode material is a thiophene based polymer with the covalently linked sulfur species.

13) The cathode material of claim 9, wherein the conducting polymer are covalently-derivatized with sulfides and/or sulfide-containing groups.

14) A cathode material for use in a sulfur-based Lithium battery containing an electrolyte comprising, a sulfur species including sulfide components and a conducting polymer wherein the conducting polymer is a single component sulfur-based conducting polymer wherein physical constraints of the conducting polymer and the sulfide components via covalent bonds which are present regardless of charge state of the cathode material.

15) An electric current producing cell comprising:

- a) an anode;
- b) a cathode containing a cathode material of claim 14; and,
- c) an electrolyte between the anode and cathode.

16) An electric current producing cell comprising:

- a) an anode;
- b) a cathode containing a cathode material of claim 12; and,
- c) an electrolyte between the anode and cathode.

17) An electric current producing cell comprising:

205040 6250650

- a) an anode;
- b) a cathode containing a cathode material selected by the method of claim 2; and
- c) an electrolyte between the anode and cathode.

18) The cathode material of claim 13, wherein the sulfur-derivatized conducting polymer is represented by a formula  $(R_i)_n(Y_jA_k)_m$  (where R is monomer or oligomer units of the conducting polymer, i is 1 to n and n is greater than 20, Y is a functionalizing group that provides additional physical or chemical properties to the conducting polymer and j is 0 to n; A is the sulfur species, k is 1 to n and m is 1 to 12).

19) The cathode material of claim 18, wherein n is greater than 1000.

20) The cathode material of claim 19, wherein n is greater than 100,000.

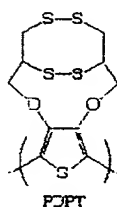
21) The cathode material of claim 13, wherein the sulfur-derivatized conducting polymer represented by a formula  $(R)_n(YS_m)_x$  (where R is a conducting polymer backbone and n is greater than 20; Y is a functionalizing group; S is an organosulfur moiety, m is 1 to 12 and x is 1 to 4).

22) The cathode material of claim 21, wherein n is greater than 1000.

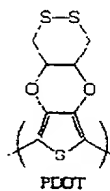
23) The cathode material of claim 22, wherein n is greater than 100,000.

24) The cathode material of claim 21, wherein R is polythiophene or its derivatives.

25) The cathode material of claim 24, wherein the single component sulfur-based conducting polymer is represented by:



26) The cathode material of claim 24, wherein the single component sulfur-based conducting polymer is represented by:



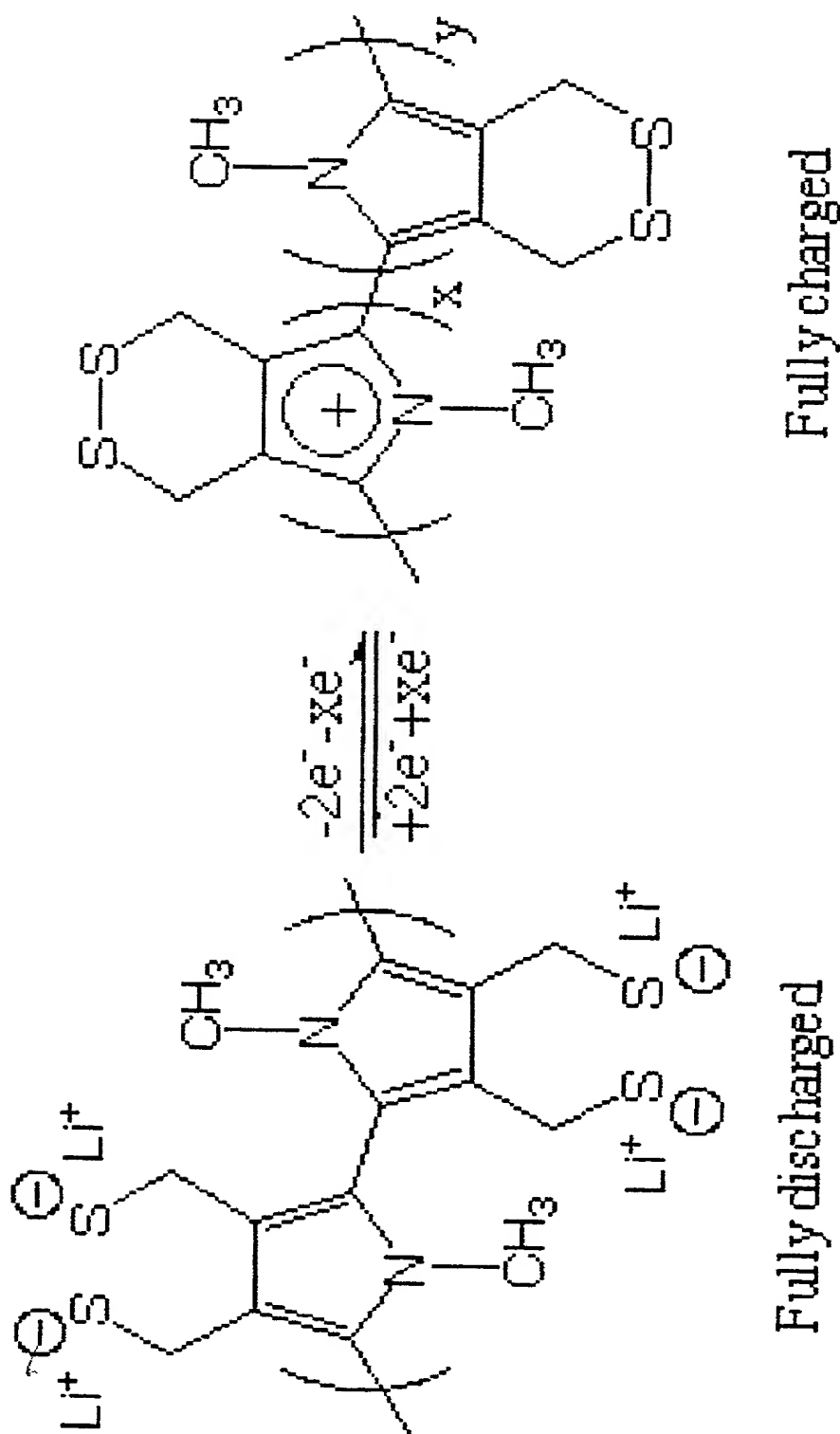


Figure 1

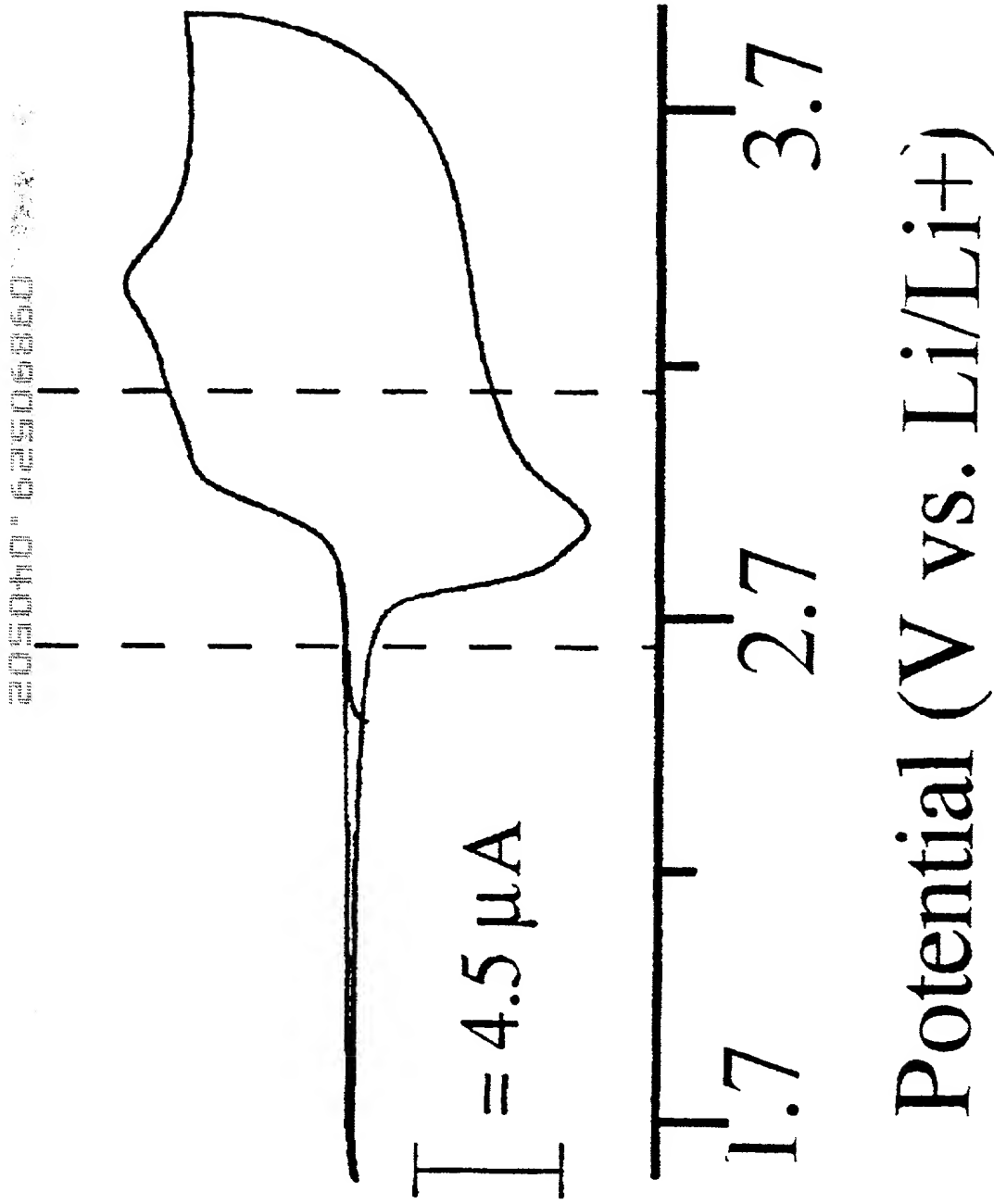


Figure 2

005040 62506860

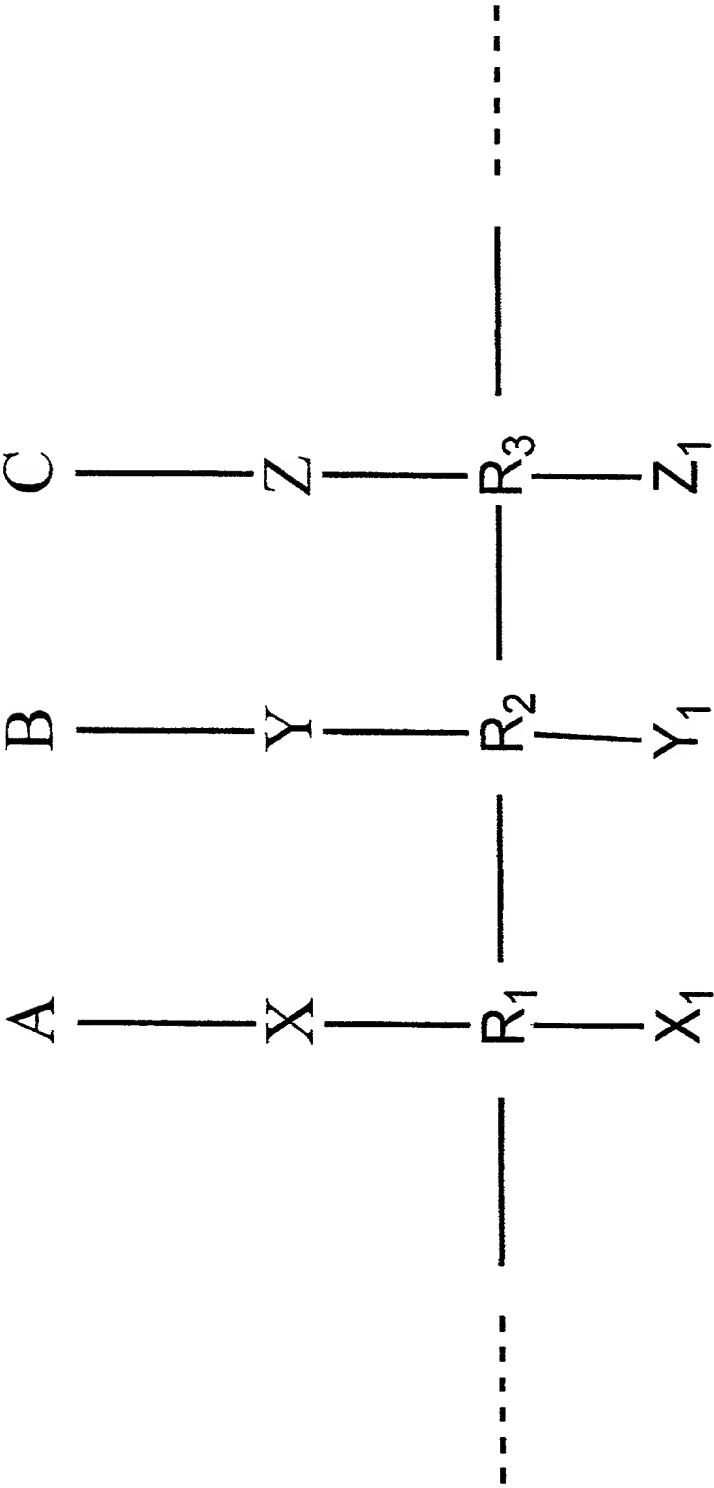


Figure 3

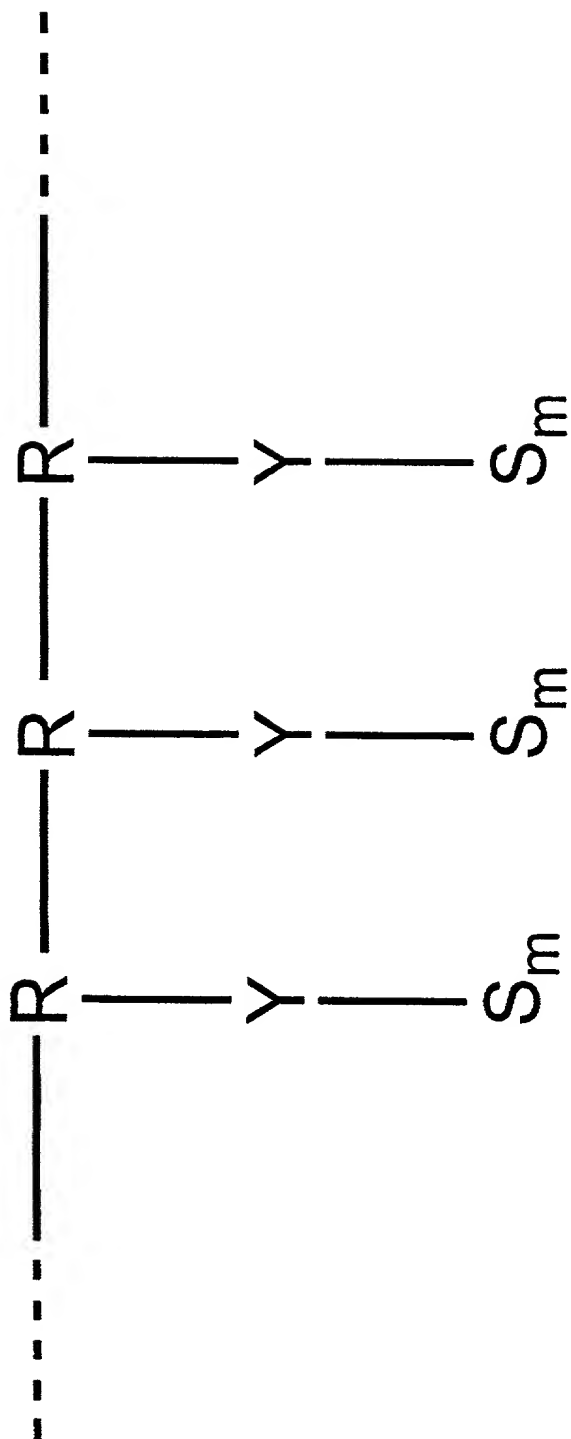


Figure 4

205040 " 62506360

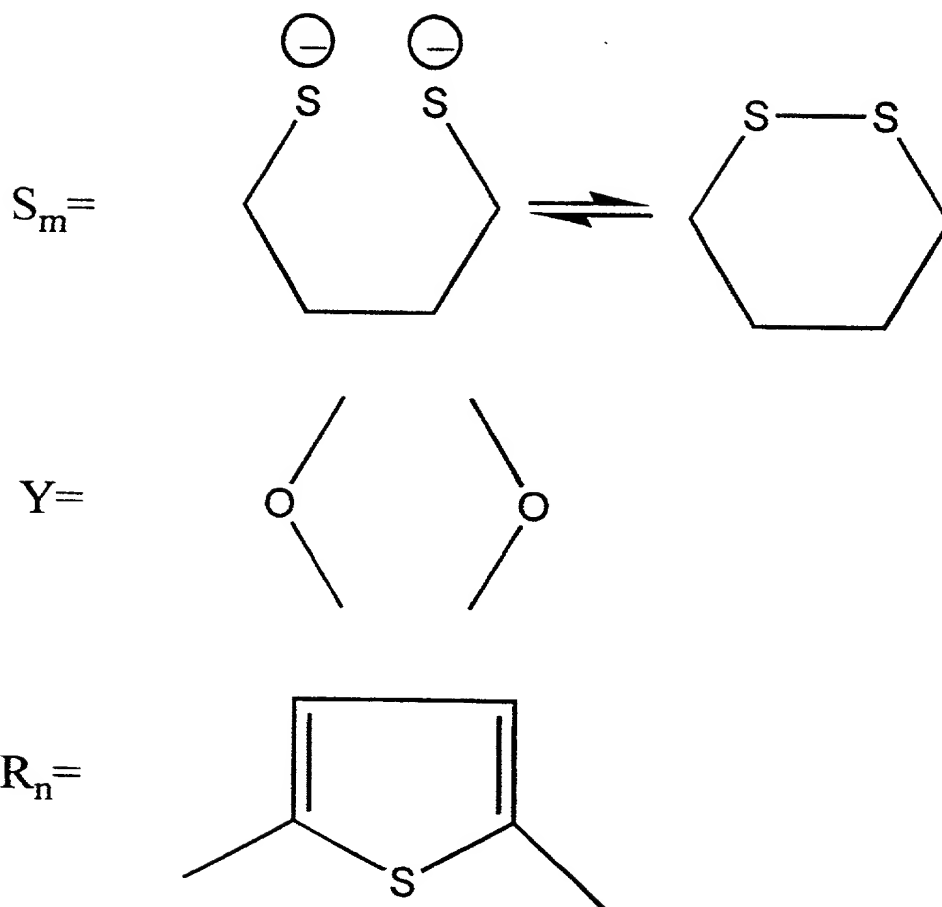
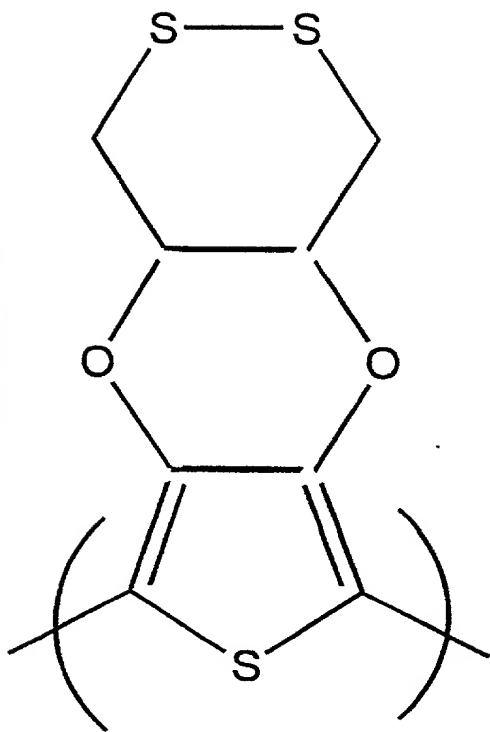


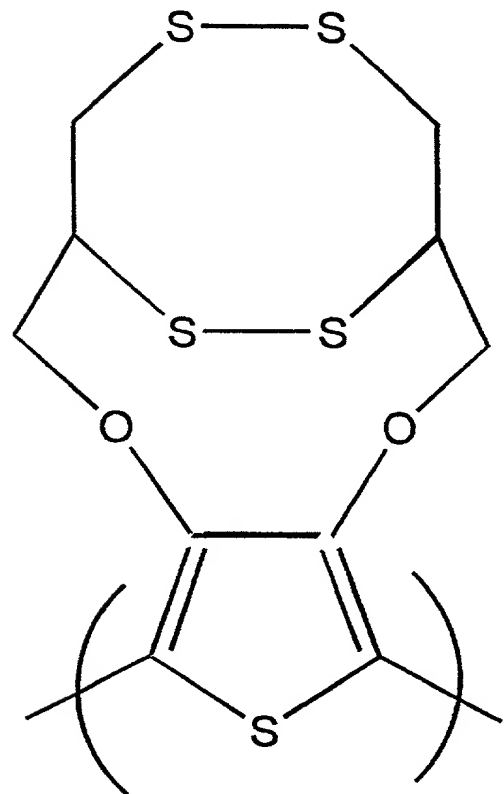
Figure 5



205040" 62505360



PDDT



PDPT

Figure 6

#20

<b>COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY</b> (includes Reference to PCT International Applications)			<b>ATTORNEY'S DOCKET NUMBER</b> 2215/50186
As a below named inventor, I hereby declare that:  My residence, post office address and citizenship are as stated below next to my name.  I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:			/
<b>SINGLE COMPONENT SULFUR-BASED CATHODES FOR LITHIUM AND LITHIUM-ION BATTERIES</b>			
the specification of which (check only one item below):			
<input type="checkbox"/> is attached hereto.			
<input type="checkbox"/> was filed as United States application			
Serial No. _____			
on _____			
and was amended			
on _____ (if applicable).			
<input checked="" type="checkbox"/> was filed as PCT international application			
Number <u>PCT/US00/02445</u>			
on <u>31 January 2000</u>			
and was amended under PCT Article 19			
on _____ (if applicable).			
I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.			
I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.55(e).			
I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:			
<b>PRIOR FOREIGN/PCT APPLICATION(S) AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. 119:</b>			
<b>COUNTRY</b> (if PCT indicate PCT)	<b>APPLICATION NUMBER</b>	<b>DATE OF FILING</b> (day, month, year)	<b>PRIORITY CLAIMED</b> <b>UNDER 35 USC 119</b>
USA	60/118,068	1 February 1999	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No
			<input type="checkbox"/> Yes <input type="checkbox"/> No
			<input type="checkbox"/> Yes <input type="checkbox"/> No
			<input type="checkbox"/> Yes <input type="checkbox"/> No
			<input type="checkbox"/> Yes <input type="checkbox"/> No

205040 62506860

Combined Declaration For Patent Application and Power of Attorney (Continued) (includes Reference to PCT international Applications)				ATTORNEY'S DOCKET NUMBER 2315/50186	
I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that/those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application(s) and the national of PCT international filing date of this application:					
PRIOR U.S. APPLICATIONS OR PCT INTERNATIONAL APPLICATIONS DESIGNATING THE U.S. FOR BENEFIT UNDER 35 U.S.C. 120					
U.S. APPLICATIONS			STATUS (Check one)		
U.S. APPLICATION NUMBER	U.S. FILING DATE	PATENTED	PENDING	ABANDONED	
PCT APPLICATIONS DESIGNATING THE U.S.					
PCT APPLICATION NO	PCT FILING DATE	U.S. SERIAL NUMBERS ASSIGNED (IF ANY)			
POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. (List name and registration number)					
Herbert I. Cantor, Reg. No. 24,302; James F. McKown, Reg. No. 25,406; Donald D. Evenson, Reg. No. 26,160; Joseph D. Evans, Reg. No. 26,269; Gary R. Edwards, Reg. No. 31,824; Jeffrey D. Sanok, Reg. No. 32,169; and William G. Ascherman, Reg. No. 45,320.					
Send Correspondence to: Crowell & Moring, L.L.P. P.O. Box 14300 Washington, D.C. 20044-4300			Direct Telephone Calls to: (name and telephone number)  (202) 628-8800		
	FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME	
20	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP	
1	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY	COUNTRY OF CITIZENSHIP	
	FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME	
20	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP	
2	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY	COUNTRY OF CITIZENSHIP	
	FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME	
20	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP	
3	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY	COUNTRY OF CITIZENSHIP	
	FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME	
20	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP	
3	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY	COUNTRY OF CITIZENSHIP	
I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.					
SIGNATURE OF INVENTOR 201		SIGNATURE OF INVENTOR 202		SIGNATURE OF INVENTOR 203	
DATE 3/3/02		DATE 3/5/02		DATE	

Combined Declaration For Patent Application and Power of Attorney (Continued) (includes Reference to PCT international Applications)				ATTORNEY'S DOCKET NUMBER 2215/50186	
I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that/these prior application(s) in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application(s) and the national of PCT international filing date of this application:					
PRIOR U.S. APPLICATIONS OR PCT INTERNATIONAL APPLICATIONS DESIGNATING THE U.S. FOR BENEFIT UNDER 35 U.S.C. 120					
U.S. APPLICATIONS			STATUS (Check one)		
U.S. APPLICATION NUMBER	U.S. FILING DATE	PATENTED	PENDING	ABANDONED	
PCT APPLICATIONS DESIGNATING THE U.S.					
PCT APPLICATION NO	PCT FILING DATE	U.S. SERIAL NUMBERS ASSIGNED (IF ANY)			
POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. (List name and registration number)					
Herbert I. Cantor, Reg. No. 24,392; James F. McKown, Reg. No. 25,406; Donald D. Evenson, Reg. No. 26,160; Joseph D. Evans, Reg. No. 26,269; Gary R. Edwards, Reg. No. 31,824; Jeffrey D. Sanok, Reg. No. 32,169; and William G. Ackerman, Reg. No. 45,320.					
Send Correspondence to: Crowell & Moring, L.L.P. P.O. Box 14300 Washington, D.C. 20044-4300			Direct Telephone Calls to: (name and telephone number)  (202) 628-5800		
	FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME	
20	1	POPE	John		
	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP	
		Laramie	USA	USA	
	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY	
		1166 N 11th Street	Laramie	WY 82070/USA	
	FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME	
20	2	BUTTRY	Dan		
	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP	
		Laramie	USA	USA	
	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY	
		1305 E. Custer Street	Laramie	WY 82070/USA	
	FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME	
20	3	WHITE	Shannon		
	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP	
		Laramie	USA WY	USA	
	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY	
		851 N. 5th Street	Laramie	WY 82070/USA	
I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.					
SIGNATURE OF INVENTOR 201		SIGNATURE OF INVENTOR 202		SIGNATURE OF INVENTOR 203	
DATE		Date		DATE	

Combined Declaration For Patent Application and Power of Attorney (Continued) (includes Reference to PCT international Applications)				ATTORNEY'S DOCKET NUMBER 2215/50186	
I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that/those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application(s) and the national of PCT international filing date of this application:					
PRIOR U.S. APPLICATIONS OR PCT INTERNATIONAL APPLICATIONS DESIGNATING THE U.S. FOR BENEFIT UNDER 35 U.S.C. 120					
U.S. APPLICATIONS			STATUS (Check one)		
U.S. APPLICATION NUMBER	U.S. FILING DATE		PATENTED	PENDING	ABANDONED
PCT APPLICATIONS DESIGNATING THE U.S.					
PCT APPLICATION NO	PCT FILING DATE	U.S. SERIAL NUMBERS ASSIGNED (IF ANY)			
POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. (List name and registration number)					
Herbert I. Cantor, Reg. No. 24,392; James F. McKeeown, Reg. No. 25,406; Donald D. Evenson, Reg. No. 26,160; Joseph D. Evans, Reg. No. 26,269; Gary R. Edwards, Reg. No. 31,824; Jeffrey D. Snook, Reg. No. 32,169; and William G. Ackerman, Reg. No. 45,320					
Send Correspondence to: Crowell & Moring, L.L.P. P.O. Box 14300 Washington, D.C. 20044-4300			Direct Telephone Calls to: (name and telephone number)  (202) 628-8800		
	FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME	
20	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP	
4	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY	
	FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME	
20	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP	
5	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY	
	FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME	
20	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP	
6	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY	
I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.					
SIGNATURE OF INVENTOR 204		SIGNATURE OF INVENTOR 205		SIGNATURE OF INVENTOR 206	
DATE 3/5/02		Date		DATE	